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MECHANOCHEMICAL REACTIONS OF ELASTOMERS WITH METALS(U)
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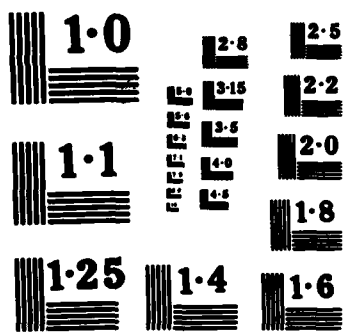
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MECHANOCHEMICAL REACTIONS OF ELASTOMERS WITH METALS

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Metal powders have been incorporated into various elastomers and the mixtures subjected to intense shearing in either an air or a nitrogen atmosphere. The molecular weight after shearing was still relatively high, however, greater than 100 kg/mole. The elastomer was then dissolved and centrifuged to remove the metal particles, and the solution was then analyzed to remove the metal particles, and the solution was then analyzed for reaction products. A strongly-UV absorbing species was formed by shearing a styrene-		

butadiene copolymer (SBR) with iron powder. The concentration increased with both the concentration of iron powder in the mixture and with the extent of shearing, and it was greater for shearing in a nitrogen atmosphere. These results are attributed to direct reaction of macromolecular radicals, formed by shearing, with the iron powder to yield an iron-polymer compound. Natural rubber (cis-polyisoprene) was found to be about as reactive as SBR, absorbing 100-200 μ g of iron per g of polymer. Polybutadiene was less reactive, and an ethylene-propylene copolymer did not react with and solubilize a significant amount of iron. Zinc was solubilized to a somewhat lesser degree, in general, than iron, while aluminum powder appeared to undergo virtually no reaction with sheared elastomers. The maximum extent of reaction (solubilization) was of the order of one metal atom per final polymer molecule, consistent with the proposed mechanism. Moreover, an analogous reaction was found to take place between simple organic radicals and iron particles in suspension.

Introduction

The wear of metal sliders in contact with soft elastomeric solids has been accounted for by a still-hypothetical mechanism. Macromolecular radicals are assumed to be generated by fracture of polymer molecules in the surface under the action of frictional shearing forces. These radicals then undergo reaction with atmospheric oxygen, or with each other, or with other macromolecules, or, if they are sufficiently long-lived, with the metal slider itself, leading to removal of metal atoms in the form of a metal-polymer compound(1-3). This hypothetical process accounts for the principal experimental observations: that the wear of metal sliders is much greater in an inert atmosphere when the macromolecular radicals cannot react with atmospheric oxygen and be stabilized in this way; and that the wear is much greater when the polymeric material forms relatively long-lived resonance-stabilized radicals upon main-chain fracture(2,3). Indeed, it is difficult to explain the wear of hard metals by soft elastic solids except in terms of some form of chemical attack.

Nevertheless, there is little, if any, direct evidence for reaction of macromolecular radicals with metal surfaces. Paneth and colleagues established that methyl radicals will react readily with a lead mirror to form the volatile product, tetramethyl lead (4,5). Tin, bismuth, mercury and cadmium compounds have also been synthesized by direct reaction of free radicals with metals (6).



There is also a great deal of evidence for the production of macromolecular radicals when polymeric solids are subjected to mechanical stresses, either in solution or in bulk, to the point of molecular rupture (7-9). Such mechanically-generated radicals have been used to make graft copolymers and interpolymers and to incorporate radical acceptors as chain endgroups (9). However, the present authors know of no previous work on the reaction of macromolecular radicals with metal surfaces.

In view of the technical importance of possible reactions between polymeric materials and metal surfaces in sliding contact; for example, in processing operations and in adhesion, friction and wear; it seems worthwhile to attempt to study such reactions directly. A series of model experiments has therefore been carried out. Metal powders (iron, zinc and aluminum) have been incorporated into representative elastomeric materials and the mixtures subjected to intense mechanical shearing. Analysis of the products has revealed that, at least in some cases, metal-polymer compounds were formed, although it has not proved possible, as yet, to identify these compounds explicitly. Different polymer and metal combinations were found to behave quite differently. These experiments, and the analytical results obtained, are described below.

Experimental

(i) Materials

Metal powders were obtained from Goodfellow Metals Ltd. The zinc powder was found by microscopy to consist of roughly spherical particles having a mean diameter of about 4 μm . The iron and aluminum powders consisted of metal platelets, 10-70 μm in length and width and 4 - 6 μm in thickness. The elastomers employed were: natural rubber (SMR - 5L, cis - polyisoprene); styrene-butadiene rubber (FRS-1502, Firestone Tire and Rubber Company, 23.5/76.5 styrene/butadiene copolymer); polybutadiene (Diene 35 NFA, Firestone Tire and Rubber Company, 36 percent cis, 54 percent trans and 10 percent vinyl polybutadiene); and ethylene-propylene rubber (Vistalon 404, Exxon Chemical Company, 50/50 ethylene/propylene copolymer).

(ii) Mixing and Shearing

Metal powder was added to a sample of an elastomer in a Brabender Plastograph mixing head with a 30 ml capacity. The proportions employed were generally three parts by weight of metal to one part of elastomer. Incorporating and dispersing the powder took about one minute. The mixture was then sheared for a further 15 minutes, in general, and then collected and analysed as described below. For shearing experiments in a nitrogen atmosphere the mixing head was placed in a polyethylene bag. Nitrogen was then flushed through the bag under positive pressure at a rate of about 25 l/min for 30 min before shearing began, as well as during the period of shearing.

(iii) Analytical techniques

(a) Spectroscopy

After shearing, the samples were dissolved in reagent-grade heptane at a concentration of about 2.5 percent and centrifuged to remove the suspended metal particles. Samples were also sheared without any metal powder being added, dissolved and centrifuged in the same way to provide reference spectra. Ultraviolet-visible spectra were then obtained by difference, using the control solution as a reference, over a wavelength range of 190 to 500 nm.

(b) Elemental analysis

Two methods were employed to determine the amount of iron taken up by the elastomers. The first is based on that developed by Thompson for iron analysis in foods (10). Reference solutions of ferric nitrate were first prepared by dissolving iron powder in nitric acid and diluting to yield concentrations of 1, 2, 5 and 10 ug of iron per ml. A calibration curve was then prepared using these reference solutions, as follows. Using 25 ml samples in a separation funnel, 5 ml of concentrated HCl, 1 ml of $K_2S_2O_8$ and 10 ml of 20 percent KSCN were added with swirling. Then, 20 ml of heptane was added, and the mixture shaken for 30 sec and allowed to separate. After this, 25 ml of isobutyl alcohol was added and the mixture shaken for a further 2 minutes and allowed to separate again. The aqueous layer was then removed and discarded and about 100 mg of anhydrous sodium sulfate was added to the remaining organic portion to remove any remaining water.

After standing overnight, the percent transmittance of the solutions at 485 nm was measured. A calibration plot was then constructed in the form: \log_{10} transmittance (percent) versus iron concentration in the original sample.

The concentration of iron in a sample of elastomer was determined by means of this calibration curve, using transmittance measurements on solutions prepared with the reference iron solution replaced by an equal amount of water and the added heptane replaced by a solution of the elastomer in heptane. Reagent blanks, which contain neither polymer nor added iron, and controls, which contain no added iron, were included in the analysis.

The second method employed for determining the amount of metal incorporated into the elastomer was atomic absorption spectrometry using a Varian Model AA-975 spectrometer, operating in the flame absorbance mode. Again, calibration curves were constructed using reference solutions of each metal in HCl and measuring their absorbance. Aqueous solutions were prepared from the elastomer samples dissolved in heptane by adding 5-10 ml of 50 percent HCl to a 20 ml sample in a separation funnel, shaking the mixture for 30 sec and then allowing it to separate. The aqueous portion was then collected and the extraction procedure repeated twice more on the organic portion. The three aqueous portions obtained in this way were combined for the subsequent measurement of absorbance.

(c) Polymer molecular weight

The molecular weight of elastomer samples was determined after shearing from measurements of their intrinsic viscosity.

Toluene at 25°C was used as the solvent for NR, SBR and BR; cyclohexane at 40°C was used for EPR. Values of the coefficients K and a in the Mark-Houwink equation relating intrinsic viscosity to molecular weight M , $[\eta] = K M^a$, were taken from the literature (11,12); they are given in Table 1.

Results and discussion

(i) Qualitative observations: SBR with iron powder.

Figure 1 shows the ultraviolet-visible spectra of samples of styrene-butadiene rubber (SBR) which have been subjected to intense shearing with and without iron powder being present. Strong absorbances are noted at 300 nm and below 270 nm for the control sample. These absorbances are not observed in the difference spectra, however. Using the control sample as a reference, a new absorbance is found at 340 nm for the samples which were sheared with iron powder. It is noteworthy that some iron-containing organic compounds (e.g., some substituted ferrocenes) have absorbances in this region (13).

If this new absorbance is, indeed, due to a reaction product with iron, then a change in the amount of iron present should have an effect on the absorption intensity. The upper curve in Figure 1 is the difference spectrum for a sample sheared with 300 parts by weight of iron powder and it clearly exhibits a more intense absorption than the sample with 100 parts.

The new absorbance peak might arise merely from suspended iron particles in the polymer solution and not from a new iron-polymer compound. To test this possibility, iron powder was suspended in a solution of SBR using a blade stirrer and the spectrum observed after centrifuging this suspension in the usual way and then re-stirring to bring ^{a small amount of} the iron powder into suspension again. As shown in Figure 2, the absorption was somewhat greater over the entire range of wavelengths but no absorbance maximum appeared at 340 nm. Thus, the new peak is not merely a result of the presence of iron particles.

In order to determine whether mechanical shearing is necessary to induce the new absorption peak, a suspension of iron powder in a polymer solution was heated to 80°C for 20 minutes under nitrogen, to simulate the heating undergone by polymer samples during shearing. No absorbance was found at 340nm after this heat treatment, as shown in Figure 2, indicating that mechanical shearing is, indeed, necessary to bring about the new absorbance.

In order to vary the extent of shearing undergone by the polymer-iron mixture, a sample was prepared by incorporating 300 parts by weight of iron powder into 100 parts by weight of SBR using the Brabender Plastograph mixing head for 2 minutes only. This sample was then passed repeatedly through the nip of a two-roll rubber mill and the ultraviolet-visible *difference* spectrum determined as a function of the number of passes, and hence of the amount of shearing that the sample had been subjected to. As shown in Figure 3, the absorbance at 340 nm increased continuously with the extent of shearing, denoted by the number of milling passes, as would be expected for a mechanochemical reaction.

It is perhaps surprising that the iron-polymer compound formed on shearing appeared to be relatively stable. A solution was irradiated in the spectrophotometer at 340 nm, the wavelength of maximum absorbance, for 24h without a significant change taking place in the intensity of absorption.

(ii) Qualitative observations: NR, BR and EPR with iron powder.

Similar experiments were carried out with mixtures of iron powder and NR, BR or EPR. The ultraviolet-visible spectra for NR mixed with 300 parts by weight of iron powder and sheared for 15 minutes is shown in Figure 4. In this case, the difference spectrum,

obtained with reference to a control sample containing no added iron powder, shows only a weak absorption peak at 310 nm. When BR and EPR were employed, no significant absorption peaks were observed in the difference spectra over the entire range of wavelengths. Thus, for these elastomers there is little or no spectroscopic evidence for the formation of an iron-polymer compound as a result of mechanical shearing.

(iii) Qualitative observations: Simple organic radicals and iron powders.

A simple model system was studied to examine the possibility of a direct reaction between organic radicals and iron powder. Benzoyl peroxide was chosen as the radical source and a relatively inert solvent, heptane, as the reaction medium. Iron powder (5g) was added to 50 ml of heptane and the suspension heated in a refluxing condenser. Benzoyl peroxide (2.5g) was added and the mixture refluxed for 12-15 h. During this period the benzoyl peroxide decomposed and an orange-red color developed in the solution.

When a mixture of iron powder and heptane was refluxed alone, the liquid remained colorless. Similarly, when benzoyl peroxide and heptane were refluxed alone, without iron powder being present, the solvent remained colorless. Thus, the strongly-colored product is formed only when benzoyl peroxide and iron powder are heated together. This suggests that an organic iron compound is formed by the reaction of simple organic radicals with iron particles.

The ultraviolet-visible spectrum of the colored reaction product is shown in Figure 5, and compared there with the spectrum obtained with a sheared mixture of SBR and iron powder. The two spectra are remarkably similar, suggesting that the product of the model reaction resembles that formed on shearing a mixture of SBR and iron powder.

Proton nuclear magnetic resonance spectra for the products of the model reaction are shown in Figure 6. Resonances observed at 1-2 ppm are attributed to the heptane solvent and that observed at 7.2 ppm is attributed to the benzene ring in the decomposed peroxide. The region of interest

is between 12 and 13 ppm where acidic ^{hydrogen} Δ resonates, because one of the decomposition products of benzoyl peroxide is benzoic acid, formed from the peroxy radical on ^{hydrogen} Δ addition. An acidic proton absorption is noted in spectrum A, when no iron was present, but it is virtually absent in spectrum B, when benzoyl peroxide was decomposed in the presence of iron powder. This suggests that peroxy radicals undergo different reactions in the presence and absence of iron powder.

(iv) Qualitative observations: zinc and aluminum powder.

Samples of SBR, NR and BR were mixed with 300 parts by weight of zinc powder per 100 parts by weight of elastomer and subjected to mechanical shearing for 15 minutes in the Brabender Plastograph mixing head. For these experiments, the mixing head was surrounded by a nitrogen atmosphere. After dissolving the samples in heptane and centrifuging the solutions to remove zinc powder, ultraviolet-visible spectra were determined using control samples as references.

The difference spectra obtained for sheared mixtures of zinc with SBR, NR and BR all showed absorbances in the range 310-360nm, with a broad maximum at around 340nm. Examples are shown in Figures 7-9. When zinc powder was merely suspended in polymer solutions, the spectra obtained showed no significant absorption over this range of wavelength. At first sight, therefore, one may conclude that a reaction has taken place between these elastomers and zinc powder as a result of mechanical shearing. However, the intensity of absorption was observed to decrease with increasing time of

centrifugation of the solutions, as shown in Figures 7-9. (No similar effect was found with iron powder, in the experiments reported above.) It seems possible that the products of reaction are strongly associated with zinc particles so that attempts to remove the particles also tend to remove the reaction products from solution.

When mixtures of SBR or NR and aluminum powder were subjected to mechanical shearing, and then dissolved and centrifuged, the solutions were found to be clear and non-absorbing in the UV-visible range when referenced to control solutions. Thus, there is no spectroscopic evidence of reaction between these elastomers and aluminum powder as a result of mechanical shearing.

(v) Quantitative analysis for iron.

The results of atomic absorption^{and colorimetric} analysis of selected SBR samples are given in Table 2. They are expressed as weight ratios of iron to polymer in the sample solutions, for easy comparison. In each case, the corresponding weight ratio for a control sample, typically 20-30 μg Fe/g of polymer, has been subtracted from the measured value to indicate the additional amount of iron incorporated into the polymer as a result of the stated treatment.

It is seen that little iron is absorbed as a result of stirring or heating a suspension at 80°C for 20 minutes. After intense shearing of a polymer-iron mixture in an air atmosphere, however, a substantial amount is found to be incorporated, and an equivalent amount of shearing in a nitrogen atmosphere caused 2-3 times as much iron to be absorbed, of the order of 0.5 atoms of iron per final polymer molecule. This observation is in accord with the proposed mechanochemical

reaction scheme in which macroradicals formed by shear-induced rupture of the polymer molecules react directly with iron to yield a polymer-iron compound. In an air atmosphere, the radicals will tend to be stabilized by reaction with oxygen and this will decrease the extent of reaction with iron.

Iron particles are undoubtedly covered with a layer of iron oxide. In order to examine the importance of this feature, the iron powder was oxidized further in an air oven at 150°C for 15 h. During this time the color of the powder changed from metallic grey to red-brown, indicating the formation of an increased amount of iron oxide. When this oxidized powder was mixed into SBR and the mixture sheared in the usual way, about the same amount of iron was solubilized as for the original powder, Table 2. This suggests either that the oxide coating is removed rapidly during mechanical shearing and reaction with macroradicals or that the reaction takes place with iron oxide itself rather than with iron. Further experiments are necessary to clarify this point.

Analytical results for the amount of iron absorbed by shearing with NR, BR and EPR are given in Table 3, together with the corresponding results for SBR, taken from Table 2, for comparison. It can be seen that a greater amount of iron is absorbed when shearing takes place in a nitrogen atmosphere for SBR, NR and BR. A significant amount is taken up in an air atmosphere by SBR and NR, but very little by BR. EPR seems relatively unreactive.

These results are wholly consistent with previous observations of the rate of wear of steel scrapers, sliding against rubber surfaces (3). SBR and NR were found to cause the most wear, which was greatly increased in an inert atmosphere. BR and EPR caused

much less wear. These differences were attributed to greater stability of the radicals formed by molecular rupture in SBR and NR, where resonance-stabilization can occur, in comparison with BR and EPR, especially in an oxygen-free atmosphere. However, the rubbery materials employed contained many other ingredients, notably carbon black, and the influence of the elastomer itself may well have been altered by these additives. It is interesting to note, therefore, that the present simple experiments, involving only elastomer and metal powder, give results of the same general form as before.

One exception may be remarked. In the present instance, NR appears to absorb more iron than SBR, whereas previously SBR was found to cause more wear of a steel slider than NR. However, the amount of molecular rupture induced by shearing NR is probably considerably greater than in SBR, especially at low temperatures, because NR undergoes shear-induced crystallization then and the molecules between crystallites are subjected to greater stress. Thus, the apparent reversal may be due to exceptionally severe shearing of NR in the present experiments.

If the proposed reaction mechanism were correct, the maximum amount of iron taken up by the polymer would be expected to lie between 1 and 2 iron atoms per final polymer molecule, tending towards the latter value as the original polymer molecules undergo a greater number of breaks. It is gratifying to note that the maximum values measured, are of this general order of magnitude, Tables 2 and 3.

(vi) Quantitative analysis for zinc and aluminum.

Results of atomic absorption analysis for zinc are given in Table 4 for solutions made from sheared mixtures of SBR, NR or BR with zinc powder. The amount of zinc found in an untreated

sample, typically about 8 $\mu\text{g/g}$ of polymer, has been subtracted from the measured values to indicate the effect of shearing. Shearing was carried out in all cases under a nitrogen atmosphere. Results are given for two periods of centrifugation in view of the large effect this had on the height of absorption peaks in UV-visible spectroscopy.

It can be seen immediately that significant amounts of zinc are taken up by SBR and a somewhat smaller amount by NR. Prolonged centrifugation does not reduce these amounts to an insignificant level. Indeed, for SBR it has little effect, suggesting that both the polymer and zinc particles are removed together. The remaining material will then retain a constant ratio of zinc to polymer, Table 4, while the amount of the zinc-polymer reaction product decreases, Figure 7.

For BR, the amount of zinc retained after prolonged centrifugation is extremely small. The results for zinc are generally similar to those found for iron, except that the ranking for SBR and NR is reversed.

Results for aluminum-elastomer mixtures, sheared under nitrogen, are given in Table 5. Again, the amount of aluminum found in an untreated sample, typically about 5 $\mu\text{g/g}$ of polymer, has been subtracted from the measured values. Virtually no reaction appears to occur; the amounts of aluminum incorporated are insignificant.

The general order of reactivity of the metals examined with the macroradicals produced by mechanical shearing is as follows: $\text{Fe} \geq \text{Zn} > \text{Al}$. This may reflect an intrinsic reactivity; for example, due to Coulombic attraction of the metal for the free radical; or it may reflect the relative ease with which the overlying oxide layer can be removed, by mechanical shear or chemical attack.

Conclusions

Iron and zinc powder react with elastomers during mechanical shear. Aluminum does not react to a significant extent. More metal reacts and is solubilized in a nitrogen atmosphere than in air.

The amount of iron or zinc taken up by the elastomer depends upon the type of macroradical produced by molecular rupture: relatively long-lived radicals (SBR and NR) are associated with greater metal pick-up compared to more reactive radicals (BR and EPR). These observations are in good accord with previous studies of the wear of metal blades sliding over rubber surfaces (2,3).

The maximum amount of iron or zinc taken up by the polymer is of the order of one metal atom per final polymer molecule. This is consistent with the formation of a metal-polymer compound by reaction of a polymer radical with the surface of a metal particle.

Simple radicals, produced by decomposing benzoyl peroxide in heptane, also appear to react with iron powder in suspension, in an analogous way.

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Table 1
Mark-Houwink Coefficients (11,12)

<u>Elastomer</u>	<u>Solvent</u>	<u>Temperature</u> (°C)	<u>Kx10⁴</u>	<u>a</u>
SBR	Toluene	25	5.2	0.67
NR	Toluene	25	5.0	0.67
BR	Toluene	25	1.9	0.76
EPR	Cyclohexane	40	3.3	0.75

Table 2: Results of iron analysis for SBR samples with 300 phr of iron powder added

<u>Experimental Conditions</u>	<u>Iron concentration $\mu\text{g/g}$ polymer</u>	<u>M (kg/mole)</u>	<u>Atoms of iron per polymer molecule</u>
	No Shear		
Control	10 ± 10	150	0.03 ± 0.03
Heated for 20 min at 80°C	10 ± 10	150	0.03 ± 0.03
	Sheared 15 min		
In air	60 ± 20	150	0.16 ± 0.06
In nitrogen	130 ± 20	150	0.35 ± 0.06
In nitrogen, centrifuged for 24 h	170 ± 20	-	-
In nitrogen, centrifuged for 72 h	160 ± 20	-	-
	Sheared 15 min with oxidized iron powder		
In air	30 ± 10	-	-
In nitrogen	150 ± 10	-	-

Table 3: Results of iron analysis

<u>Elastomer</u>	<u>Iron concentration</u> ($\mu\text{g/g}$ polymer)	<u>M</u> (kg/mole)	<u>Atoms of iron per</u> <u>Polymer molecule</u>
No shear			
SBR	10 ± 10	150	0.03
NR	1 ± 1	108	0.002
BR	8 ± 5	190	0.03
EPR	0 ± 5	130	~ 0
Sheared 15 min in air			
SBR	60 ± 20	150	0.16
NR	160 ± 20	108	0.31
BR	9 ± 9	225	0.04
EPR	-	-	-
Sheared 15 min in nitrogen			
SBR	130 ± 20	150	0.35
NR	270 ± 10	305	1.45
BR	37 ± 7	185	0.12
EPR	14 ± 3	130	0.03

Table 4: Results of analysis for zinc.

<u>Elastomer</u>	<u>Zinc concentration</u> ($\mu\text{g/g}$ polymer)	<u>M</u> (kg/mole)	<u>Atoms of zinc per</u> <u>polymer molecule</u>
	Centrifuged for 48 h		
SBR	210 ± 20	290	0.9
NR	70 ± 10	620	0.65
BR	40 ± 10	200	0.1
	Centrifuged for 192 h		
SBR	230 ± 10	290	1.0
NR	30 ± 10	620	0.3
BR	6 ± 1	200	0.02

Table 5: Results of analysis for aluminum.

<u>Elastomer</u>	<u>Aluminum concentration</u> ($\mu\text{g/g}$ polymer)	<u>M</u> (kg/mole)	<u>Atoms of aluminum</u> <u>per polymer molecule</u>
SBR	2 ± 1	210	0.02
NR	6 ± 5	480	0.1

Figure Captions

- Figure 1. UV-visible spectra of styrene-butadiene rubber. A, control sample; B, sample sheared in air with 100 parts by weight of iron, referenced to the control; C, sample sheared in air with 300 parts by weight of iron, referenced to the control.
- Figure 2. UV-visible difference spectra of styrene-butadiene rubber with suspended iron particles. A, centrifuged sample (control); B, sample with iron particles suspended; C, sample with iron particles suspended, after heating.
- Figure 3. Relative absorbance at 340 nm vs amount of shear for styrene-butadiene rubber with iron powder (300 phr).
- Figure 4. UV-visible spectra of natural rubber. A, control sample; B, sample with iron particles suspended; C, sample sheared in air with 300 parts by weight of iron, referenced to the control.
- Figure 5. A, UV-visible spectrum of the reaction products of benzoyl peroxide with iron; B, spectrum for styrene-butadiene rubber sheared with 100 parts by weight of iron.
- Figure 6. Proton Nuclear Magnetic Resonance spectra of the products of the model reaction. A, benzoyl peroxide (control); B, benzoyl peroxide plus iron.
- Figure 7. UV-visible difference spectra of styrene-butadiene rubber sheared under nitrogen with 300 parts by weight of zinc. A, 30 hours centrifuge time; B, 30 hours centrifuge time plus 72 hours standing; C, 146 hours centrifuge time; D, 260 hours centrifuge time.

Figure 8. UV-visible difference spectra of natural rubber sheared under nitrogen with 300 parts by weight of zinc. A, 30 hours centrifuge time plus 72 hours standing; B, 194 hours centrifuge time.

Figure 9. UV-visible difference spectra of polybutadiene sheared under nitrogen with 300 parts by weight of zinc. A, 30 hours centrifuge time plus 72 hours standing; B, 146 hours centrifuge time; C, 194 hours centrifuge time.

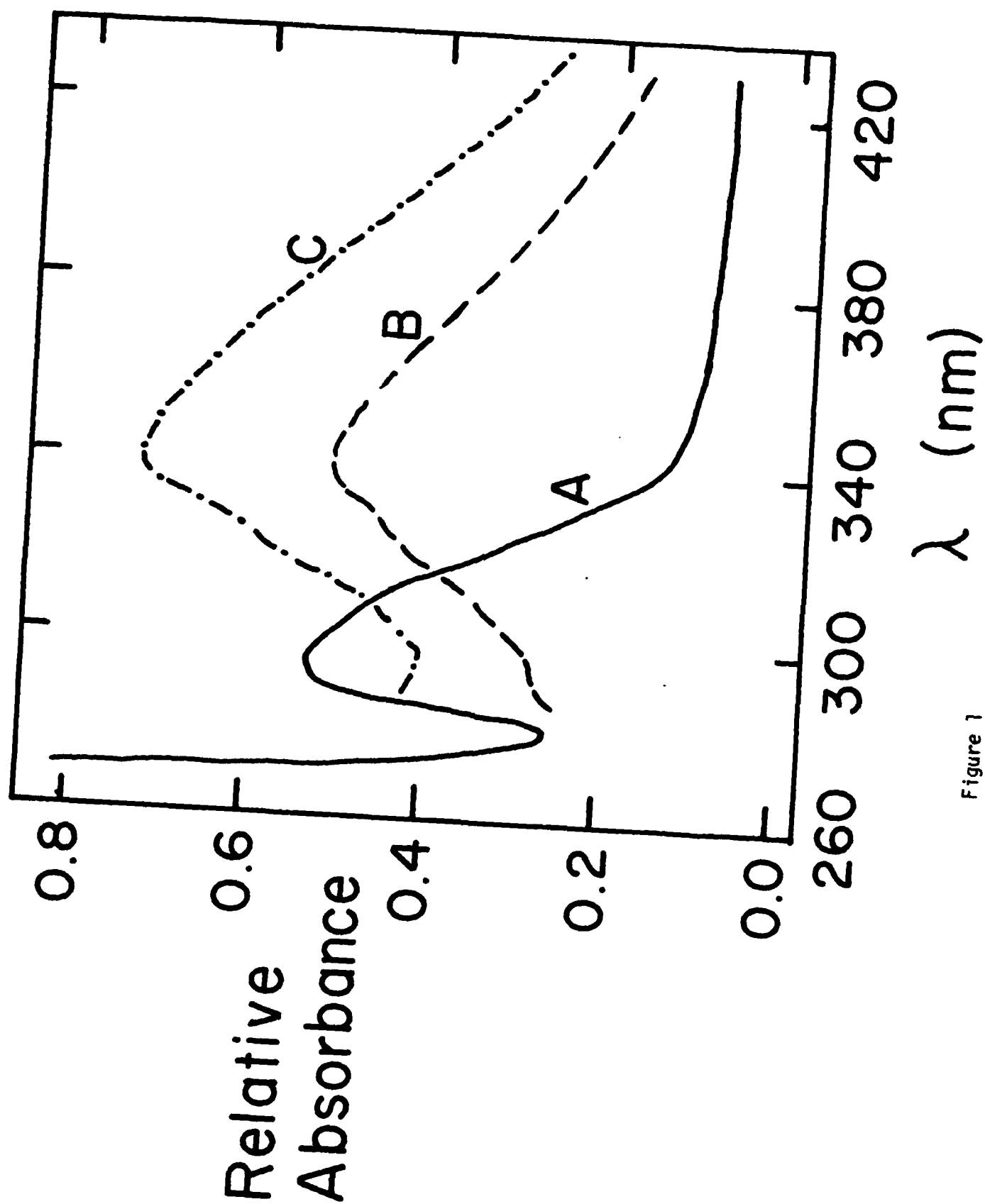


Figure 1

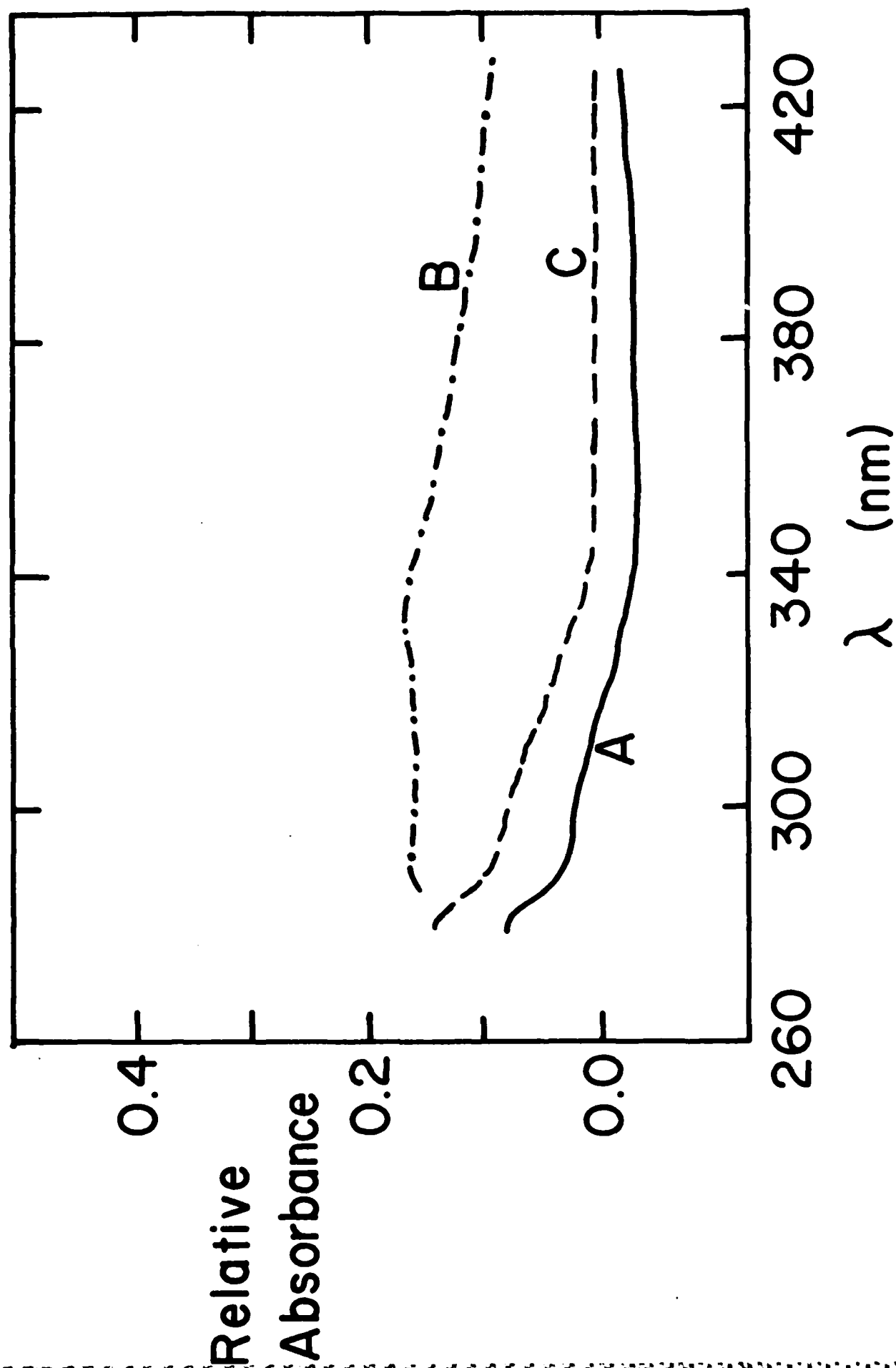


Figure 2

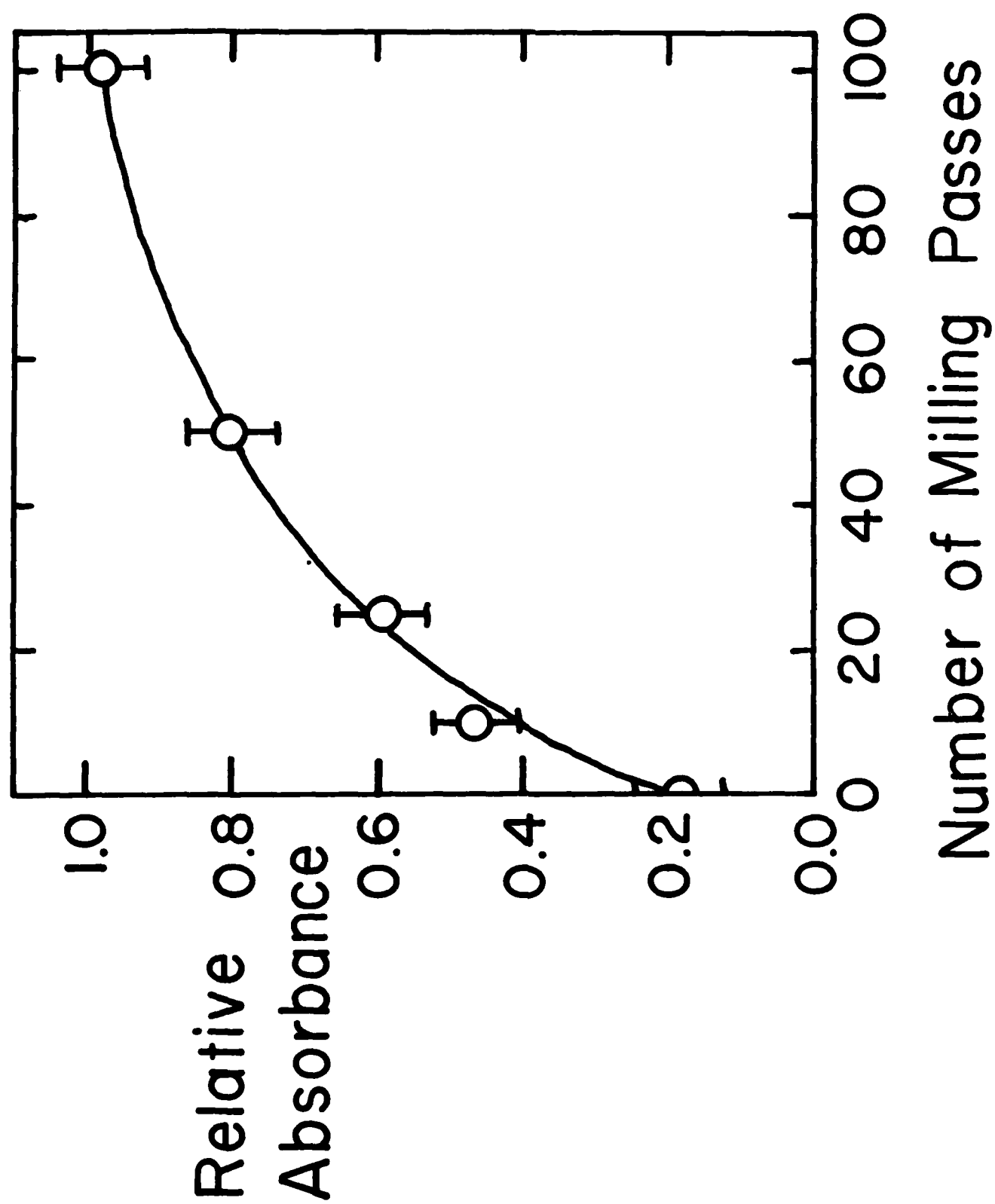


Figure 3

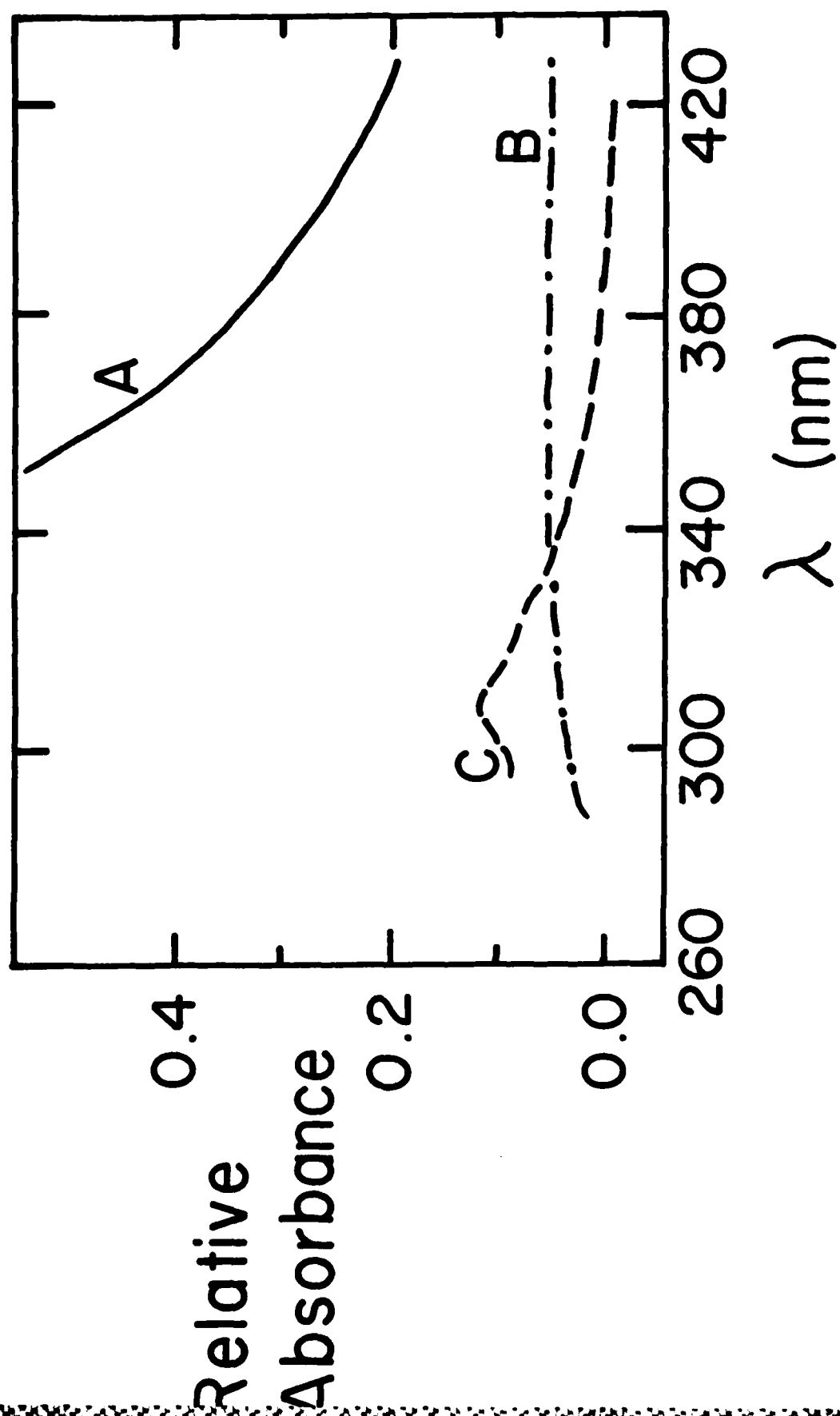


Figure 4

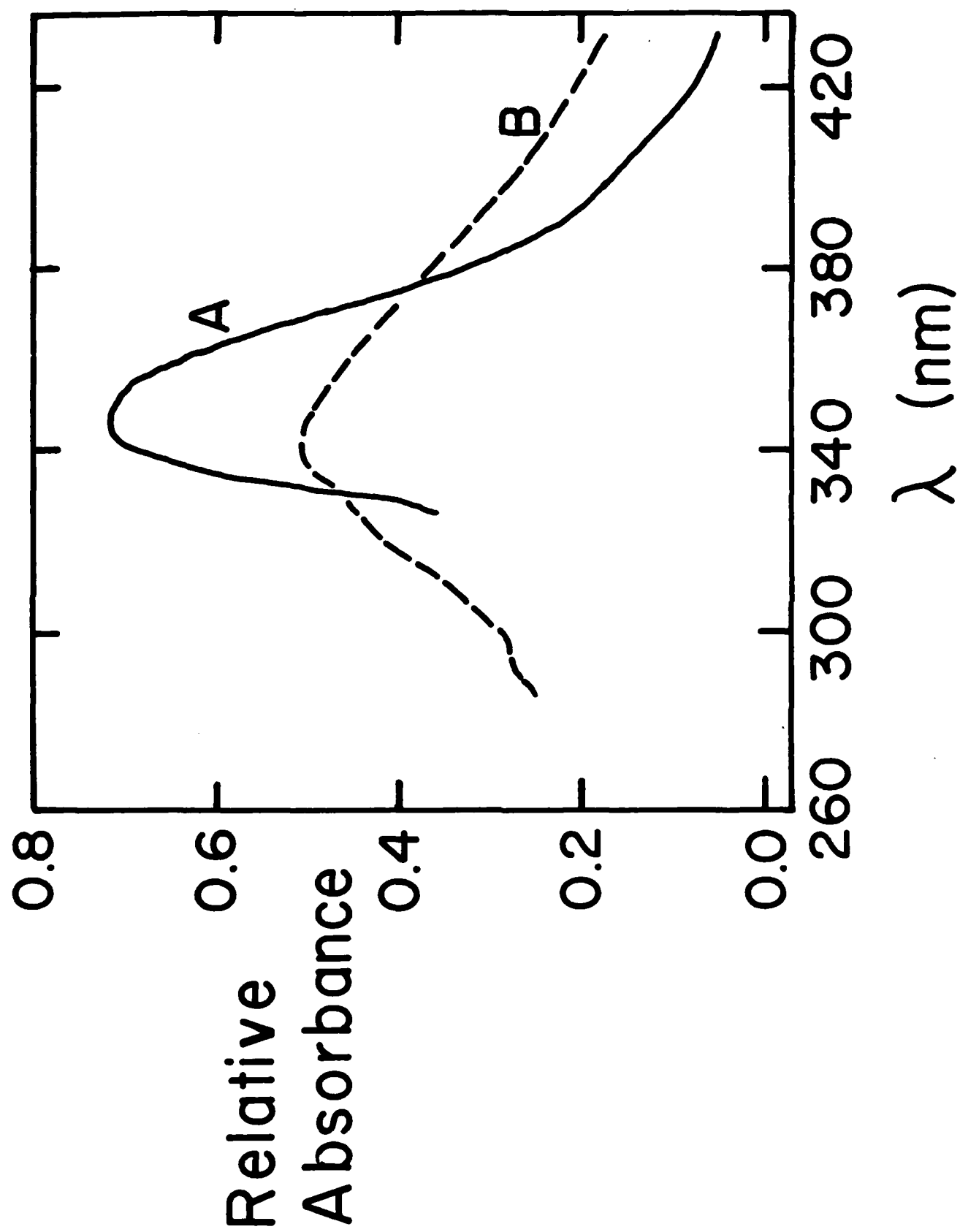


Figure 5

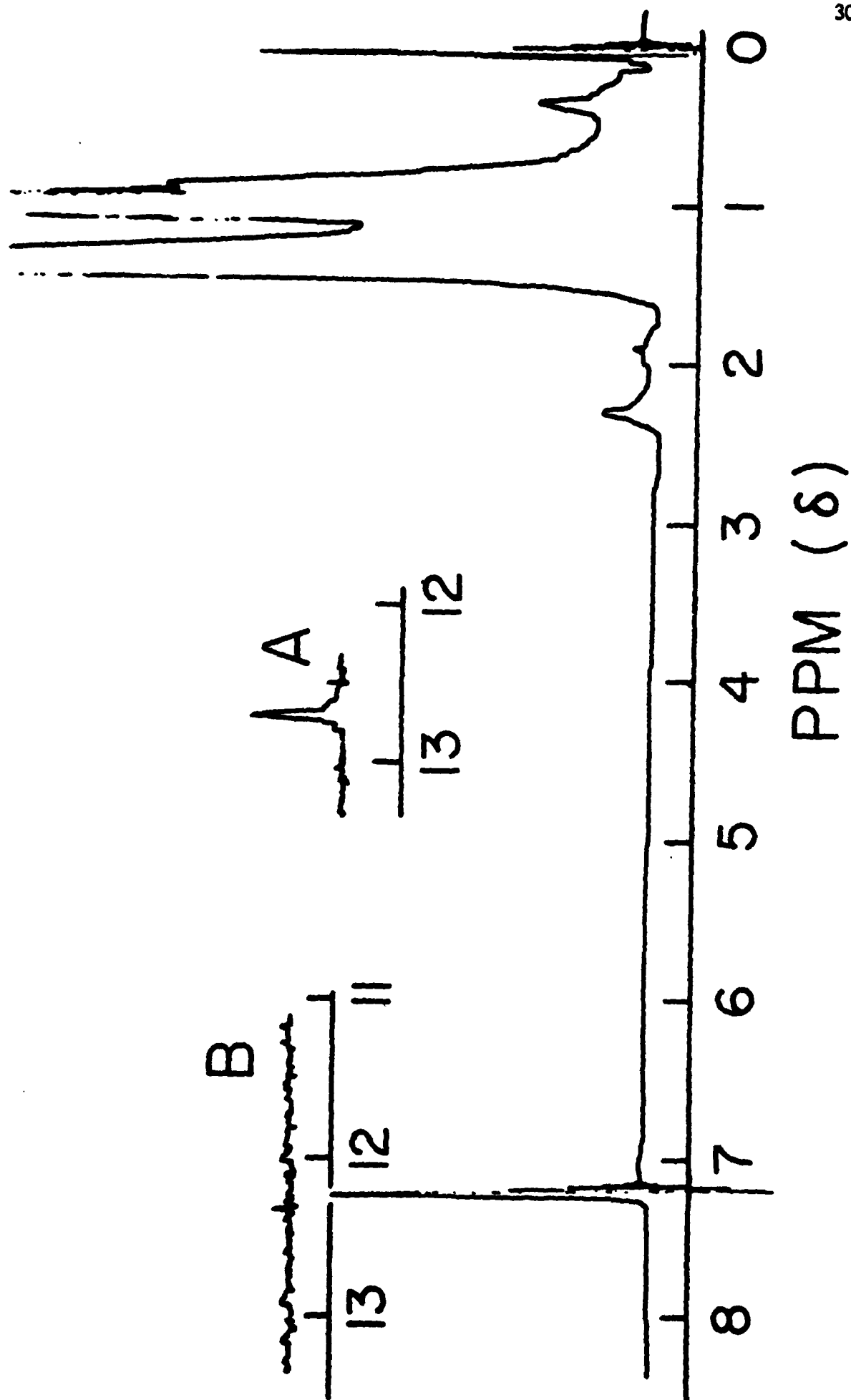


Figure 6

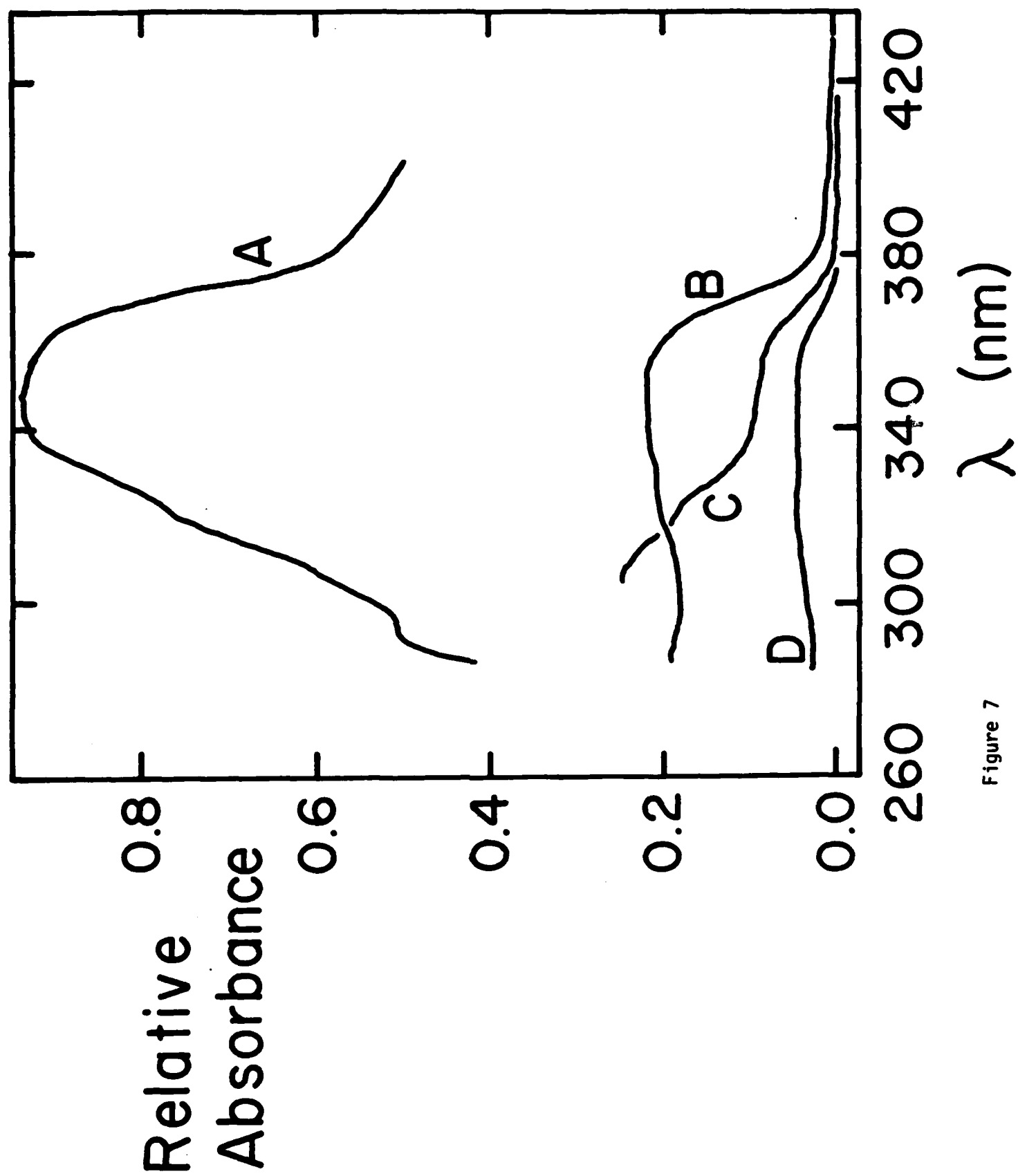


Figure 7

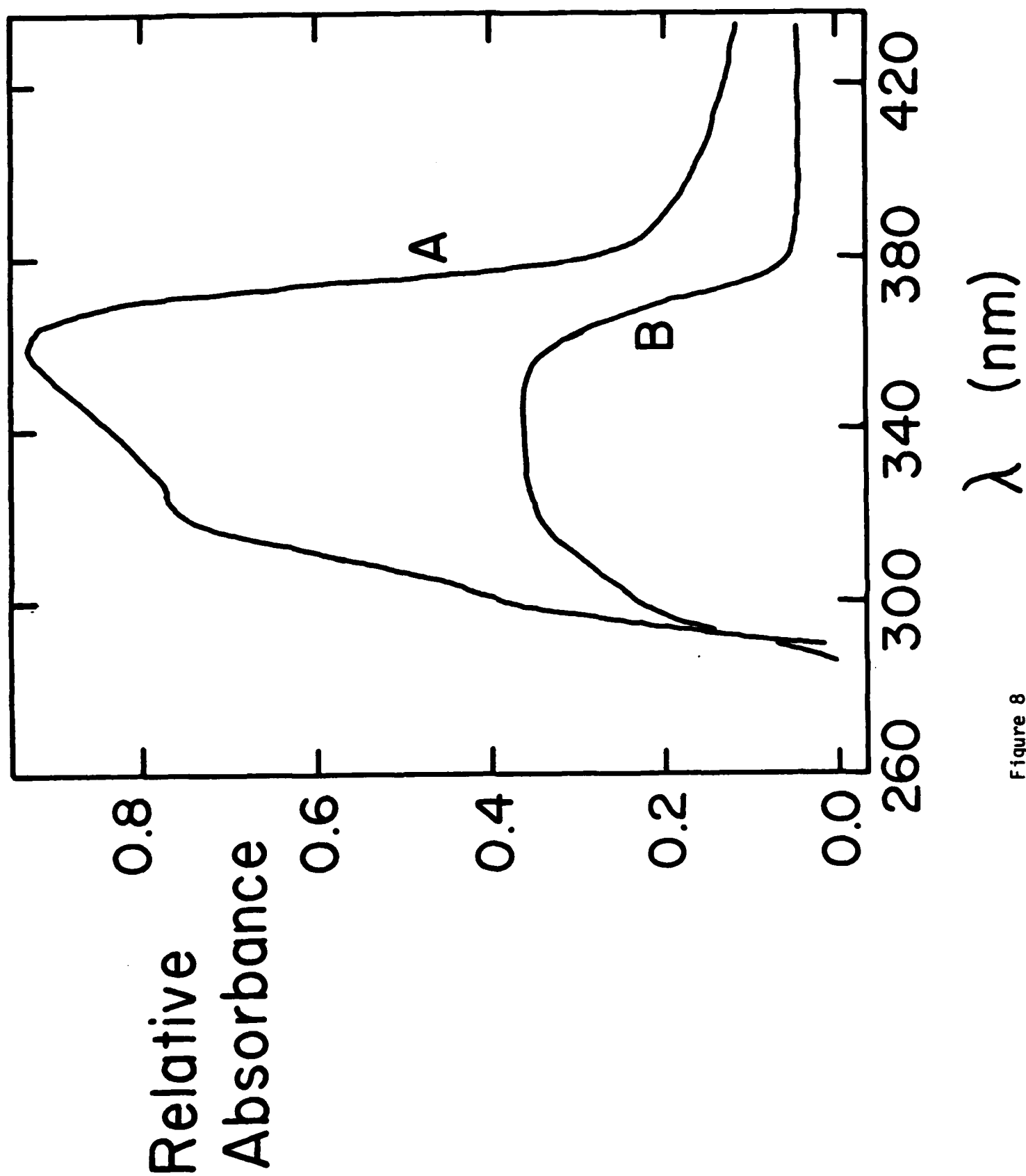


Figure 8

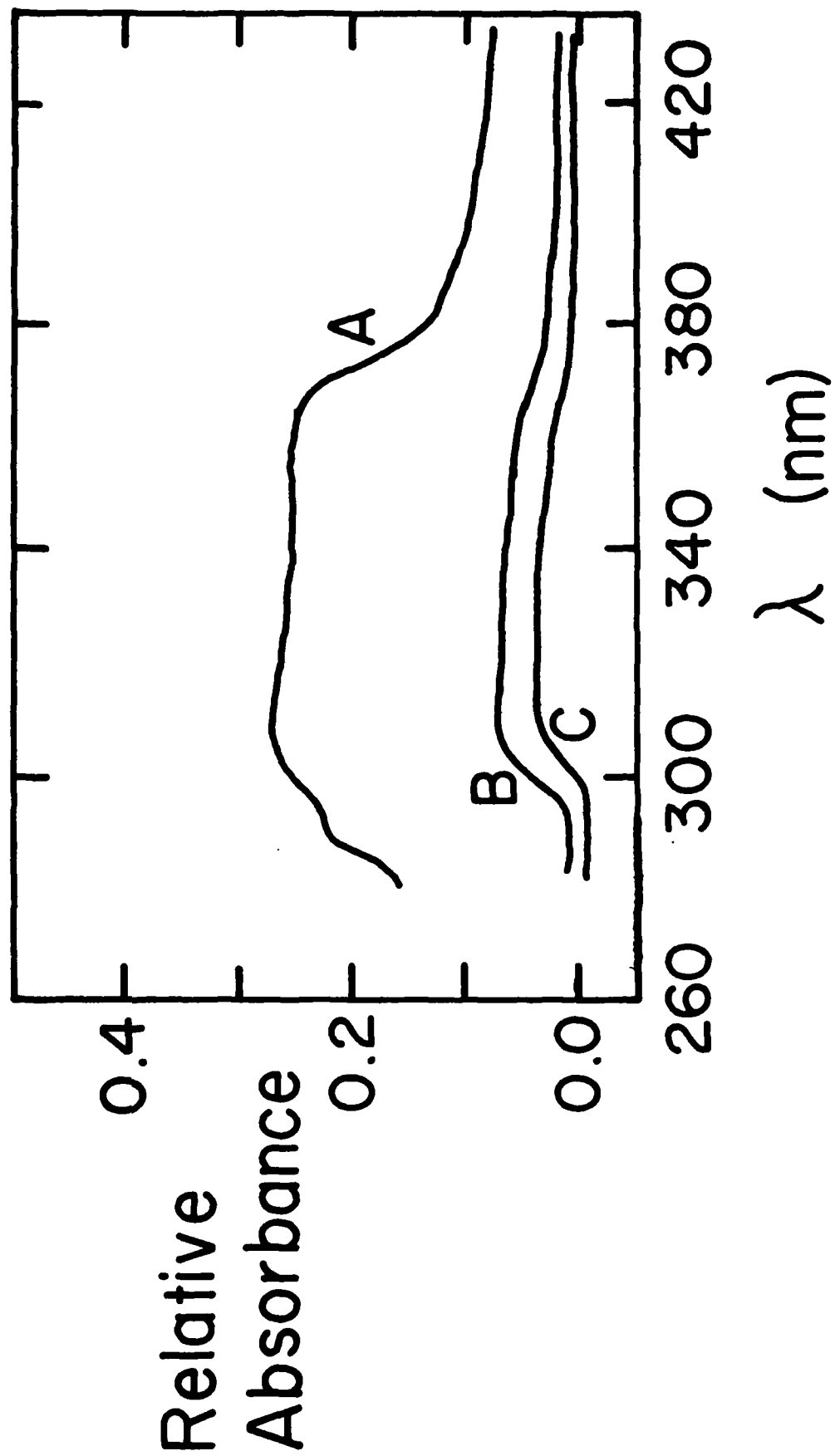


Figure 9

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